Review of Last Lecture

- Phonon spectrum in solids
- Electronic band structure
- Density of states and carrier density

Phonons Dispersion in Crystals

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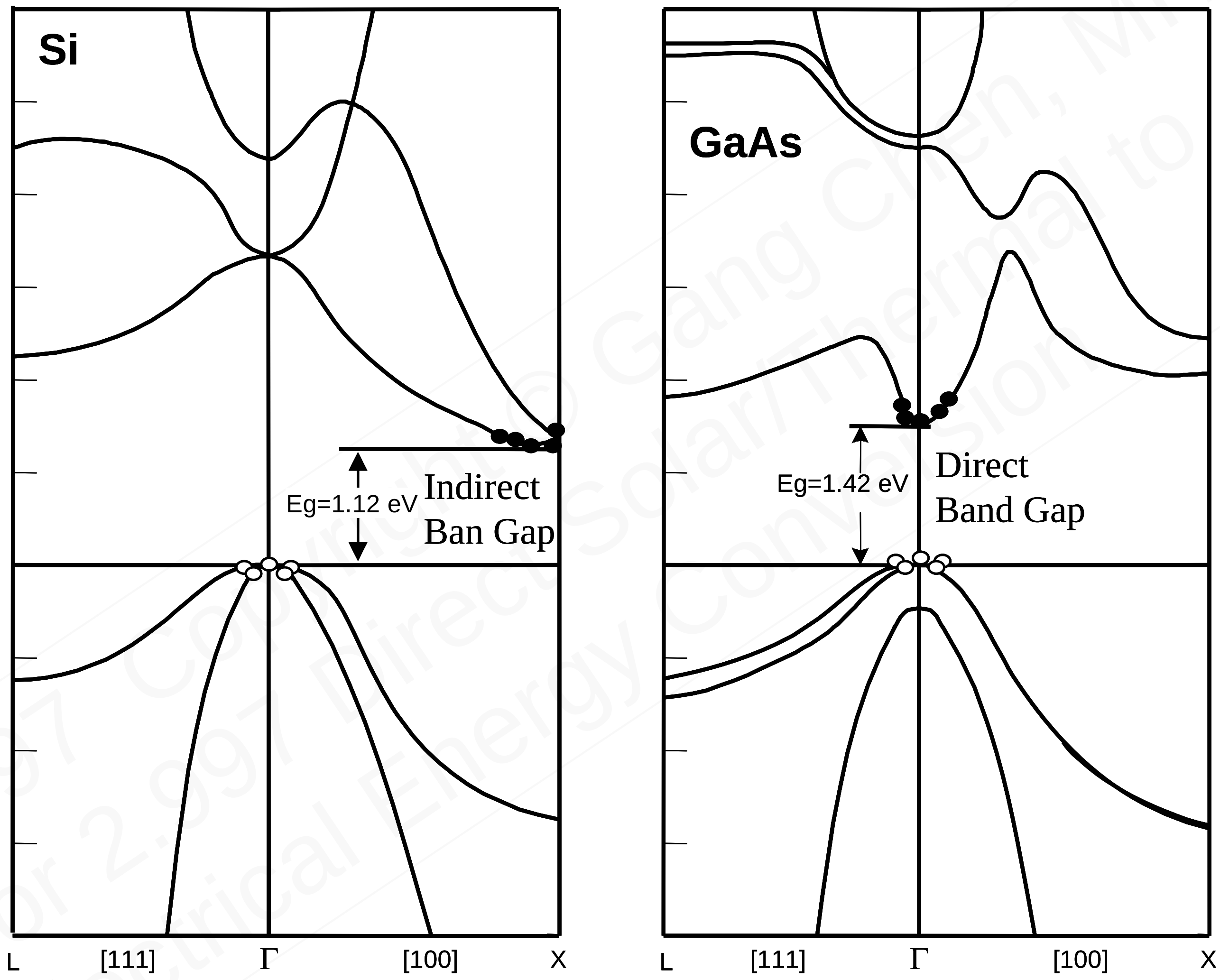
Electronic Band Structures of Real Crystals



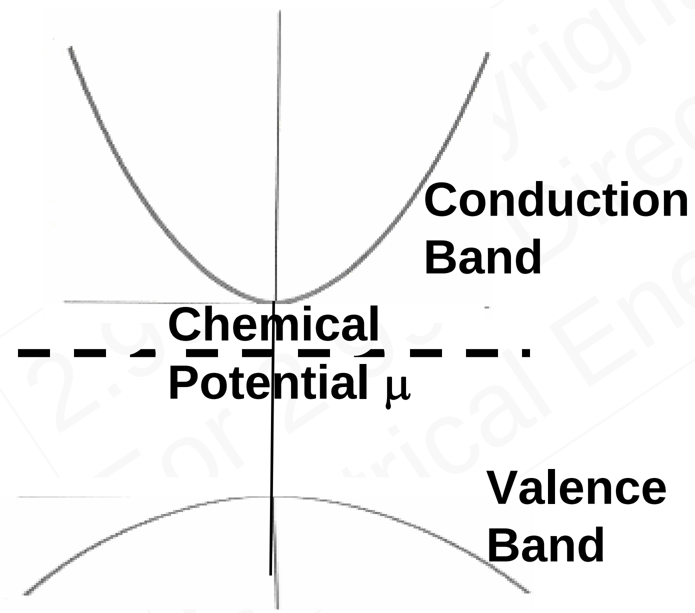
Electron Density

General:

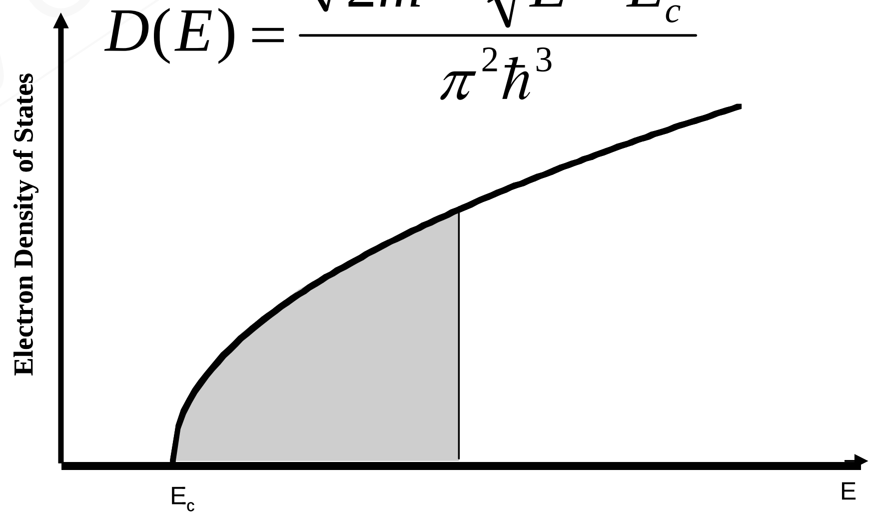
$$n = \int_{E_c}^{\infty} D(E) f(E,\mu,T) dE$$

$$n = 2\left(\frac{2\pi m^* \kappa_B T}{h^2}\right)^{3/2} \exp\left(-\frac{E_c-\mu}{k_B T}\right) = N_c \exp\left(-\frac{E_c-\mu}{k_B T}\right)$$

Under Boltzmann Statistics



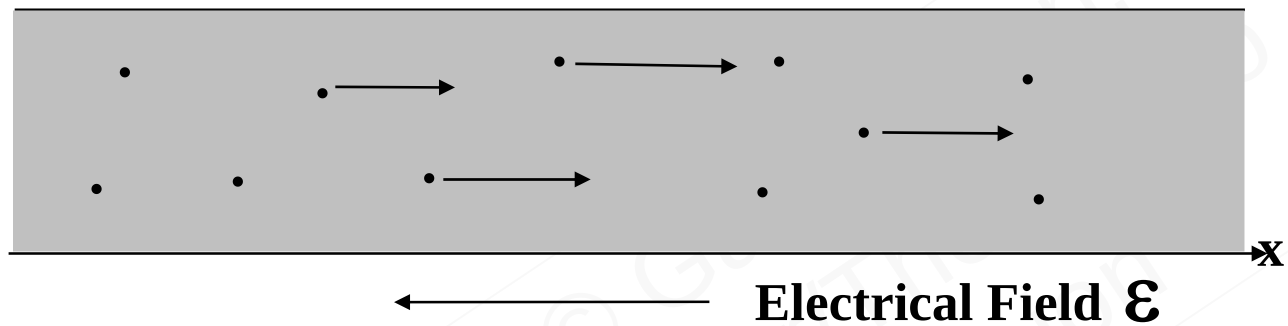
$$D(E) = \frac{\sqrt{2} m^{3/2} \sqrt{E-E_c}}{\pi^2 \hbar^3}$$



Simplified Kinetic Formulation of Thermoelectricity

Electrical Conduction

Isothermal Electrical Conductor



- Force on electrons

$$\mathbf{F} = -e\mathcal{E} = m\cdot d\mathbf{v}/dt$$

- Collision within time τ
  Drift velocity

$$\mathbf{v} = -e\tau\mathcal{E}/m = -\mu\mathcal{E}$$

- Mobility

$$\mu = \frac{e\tau}{m}$$

- Mean free path

$$\Lambda = \tau v_{th}$$

Thermal velocity

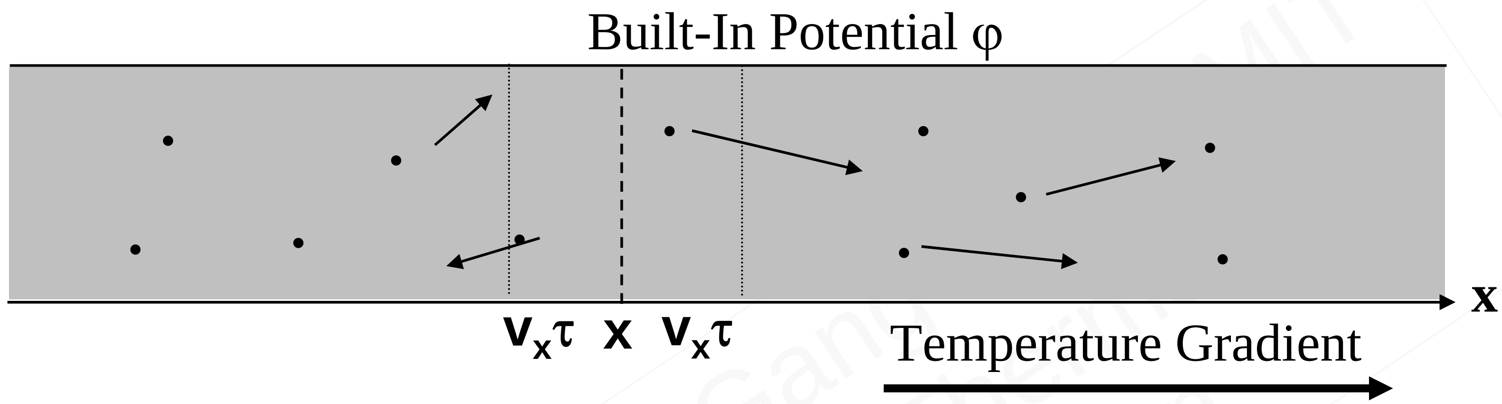
- Current density and Ohm's law

$$J_e = -en\mathbf{v} = ne^2\tau\mathcal{E}/m$$

$$J_e = \sigma\mathcal{E} = \sigma\,(-d\varphi/dx)$$

Electrostatic Potential

Coupled Charge Transport



- **Electrical current density:**

$$J_{ex} = -\frac{1}{2}\left[\left(e\mathrm{v}_{\mathrm{x}}\mathrm{n}\right)_{x-\mathrm{v}_{\mathrm{x}}\tau} - \left(e\mathrm{v}_{\mathrm{x}}\mathrm{n}\right)_{x+\mathrm{v}_{\mathrm{x}}\tau}\right] + \sigma\left(-\frac{d\varphi}{dx}\right)$$

$$= e\mathrm{v}_{\mathrm{x}}{}^{2}\tau\frac{dn}{\mathrm{dx}} + \sigma\frac{d\varphi}{dx} \qquad n = 2\left(\frac{2\pi \mathrm{m}^{*}\kappa_{\mathrm{B}}\mathrm{T}}{\mathrm{h}^{2}}\right)^{3/2}\exp\left(-\frac{E_c-\mu}{k_B T}\right)$$

$$= \frac{1}{3}e\mathrm{v}^{2}\tau\frac{n}{k_B T}\left(\frac{d\left(\mu - E_c\right)}{\mathrm{dx}} + \frac{E_c-\mu}{T}\frac{dT}{dx}\right) + \sigma\left(-\frac{d\varphi}{dx}\right)$$

$$= \sigma\left[-\frac{\mathrm{d}\varphi}{\mathrm{dx}} + \frac{1}{e}\frac{d\left(\mu - E_c\right)}{dx}\right] + \frac{1}{3}e\mathrm{v}^{2}\tau\frac{n\left(E_c - \mu + 3k_B T/2\right)}{k_B T^{2}}\left(-\frac{dT}{dx}\right)$$

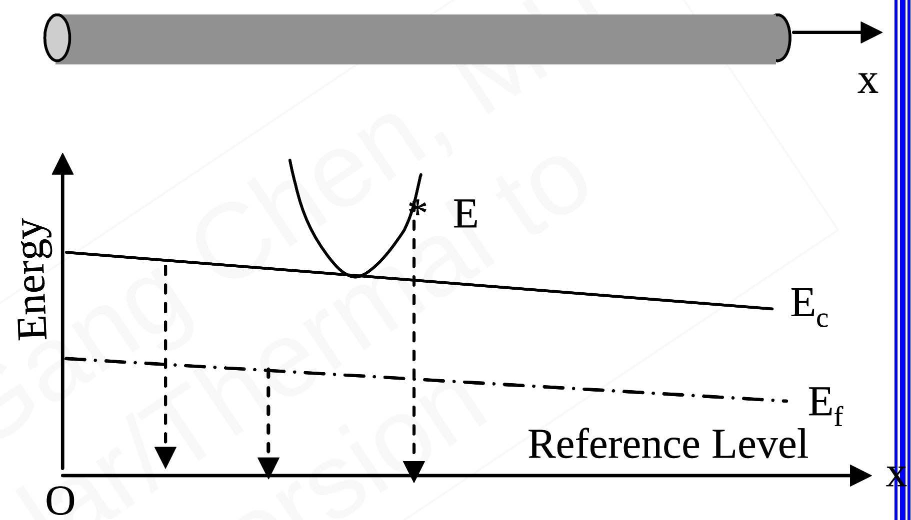
Coupled Charge Transport

$$\Phi = \varphi + \frac{\mu - E_c}{-e}$$

Chemical Potential

Electrostatic Potential

Electrochemical Potential



$$J_{ex} = \sigma\left(-\frac{d\Phi}{dx}\right) - \frac{1}{3}e\mathrm{v}^2\tau\frac{n\left(E_c - \mu + 3k_BT\right)}{k_BT^2}\left(-\frac{dT}{dx}\right)$$

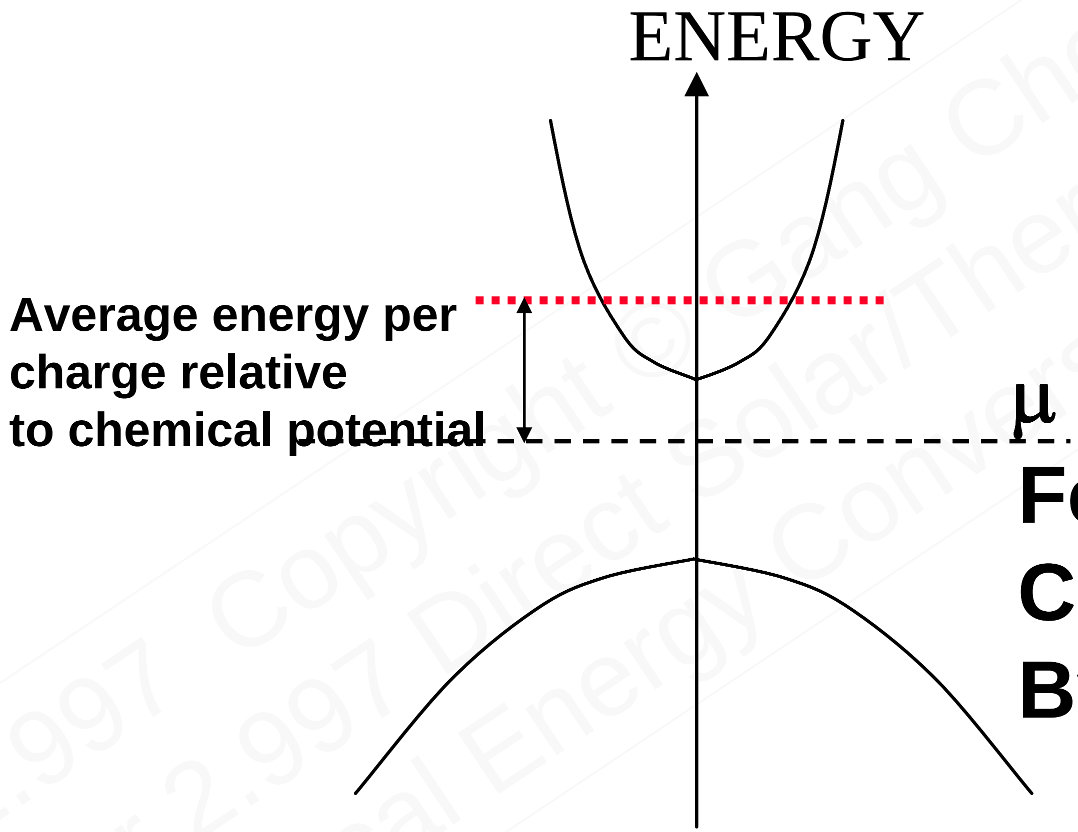
$$= \mathrm{L}_{11}\left(-\frac{d\Phi}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right)$$

- **Open Circuit J_{ex}=0 Seebeck Coefficient**

$$S = \frac{\varepsilon}{dT/dx} = -\frac{\Phi_h - \Phi_c}{T_h - T_c} = -\frac{E_c - \mu + 3k_BT/2}{eT}$$

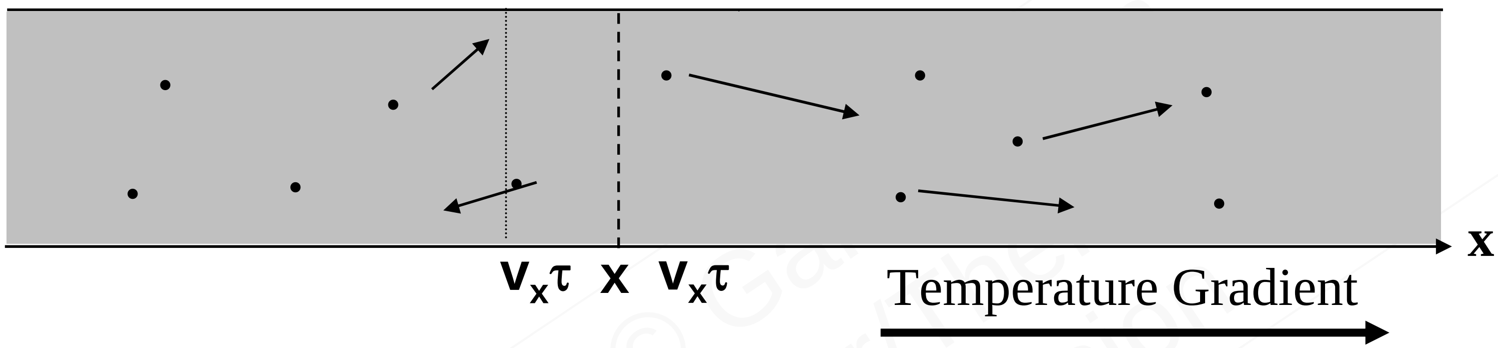
Not Accurate

Meaning of Seebeck Coefficient



Fermi Level Controlled By Doping

Heat Conduction: Diffusion Only



- Heat Flux

$$q_x = \frac{1}{2}(nuv_x)\Big|_{x-v_x\tau} - \frac{1}{2}(nuv_x)\Big|_{x+v_x\tau}$$

$$q_x = -v_x\tau\frac{d(unv_x)}{dx} = -\frac{v^2\tau}{3}\frac{dU}{dT}\frac{dT}{dx}$$

$$= -\frac{v^2\tau}{3}C\frac{dT}{dx} = -k\frac{dT}{dx}$$

——— Fourier's Law

- Thermal Conductivity

$$k = Cv\Lambda/3$$

Specific Heat (J/m³K)

Coupled Electron Heat Transport

- **Thermodynamics** $$dU = \delta q + \mu dN$$
- **Heat Carried Per Charge:** $$(E-\mu)$$
- **Electrical heat flux:**

$$J_{qx} = -\frac{1}{2}\left\{\left[(\mathrm{E} - \mu)\mathrm{v_x n}\right]_{x-\mathrm{v_x}\tau} - \left[(\mathrm{E} - \mu)\mathrm{v_x n}\right]_{x-\mathrm{v_x}\tau}\right\} + (E-\mu)\mathrm{v_d} n$$

$$= L_{21}\left(-\frac{d\Phi}{dx}\right) + L_{22}\left(-\frac{dT}{dx}\right)$$

Formal Theory

$$J_{bx}(x) = \sum_p \left[\frac{1}{V_1} \sum_{k_{x1}=-\infty}^{\infty} \sum_{k_{y1}=-\infty}^{\infty} \sum_{k_{z1}=-\infty}^{\infty} v_x\, b\, f \right]$$

Per Carrier

Distribution Function, Solving Boltzmann Eq.

b: =e current flux; = (E-μ) heat flux

$$J_{ex} = L_{11}\left(-\frac{d\Phi}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right) \qquad \left(-\frac{d\Phi}{dx}\right) = \frac{1}{L_{11}}\left[J_{ex} - L_{12}\left(-\frac{dT}{dx}\right)\right]$$

$$J_{qx} = L_{21}\left(-\frac{d\Phi}{dx}\right) + L_{22}\left(-\frac{dT}{dx}\right) \qquad J_{qx} = \frac{L_{21}}{L_{11}} J_{ex} + \frac{L_{22}L_{11} - L_{12}L_{21}}{L_{11}}\left(-\frac{dT}{dx}\right)$$

Onsager Relation: $L_{21}=TL_{12}$

Peltier Heat **Conduction Heat**

Transport Coefficients

$$L_{11} = \sigma = -\frac{e^2}{3}\int v^2 \tau \frac{\partial f_o}{\partial E} D(E) dE$$

$$L_{12} = \frac{e}{3T}\int v^2 \tau \left(E - E_f\right) \frac{\partial f_o}{\partial E} D(E) dE$$

$$L_{22} = -\frac{1}{3T}\int \left(E - E_f\right)^2 v^2 \tau \frac{\partial f_o}{\partial E} D(E) dE$$

Wiedmann Franz Law

$$L = \frac{k_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{\kappa_B}{e}\right)^2 = 2.45x10^{-8}$$

(W.Ω K^{-2})

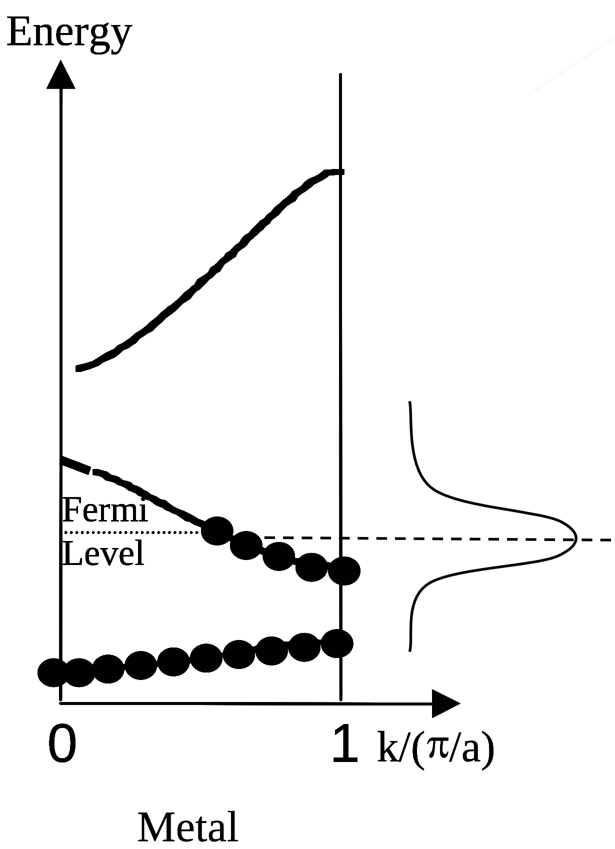
However, in semiconductors Lorentz number depends on n

Results from Formal Theory

$$S = \frac{1}{qT}\frac{\int \tau \mathbf{v}^2 D(E)(E-E_F)(-\partial f_{eq}/\partial E)dE}{\int \tau \mathbf{v}^2 D(E)(-\partial f_{eq}/\partial E)dE} = \frac{1}{q}\frac{\int (E-E_F)\sigma dE}{\int \sigma(E)dE} \propto < E - E_f >$$

$$\sigma = \frac{q^2}{3}\int \tau \mathbf{v}^2 \mathrm{D(E)}(-\partial f_{eq}/\partial \mathrm{E})\mathrm{dE}$$

Small Seebeck
Too Symmetric

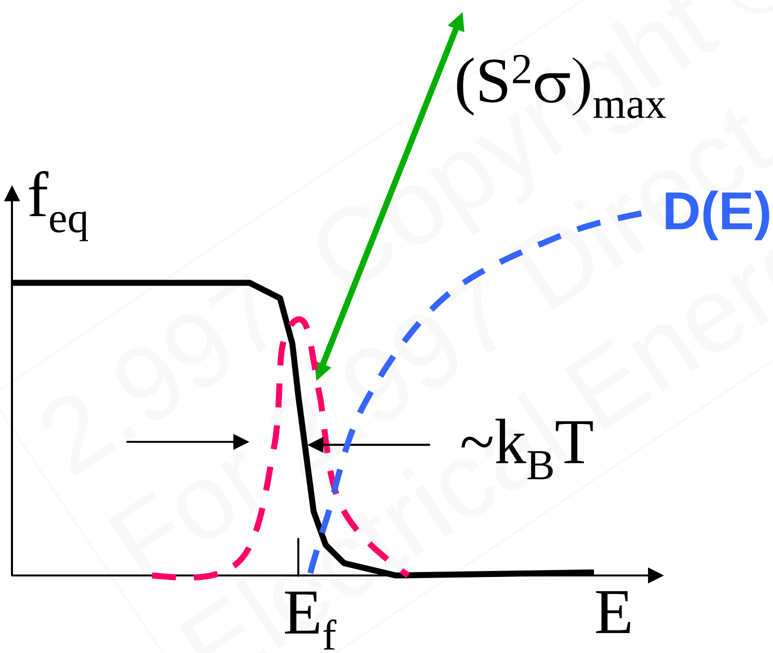


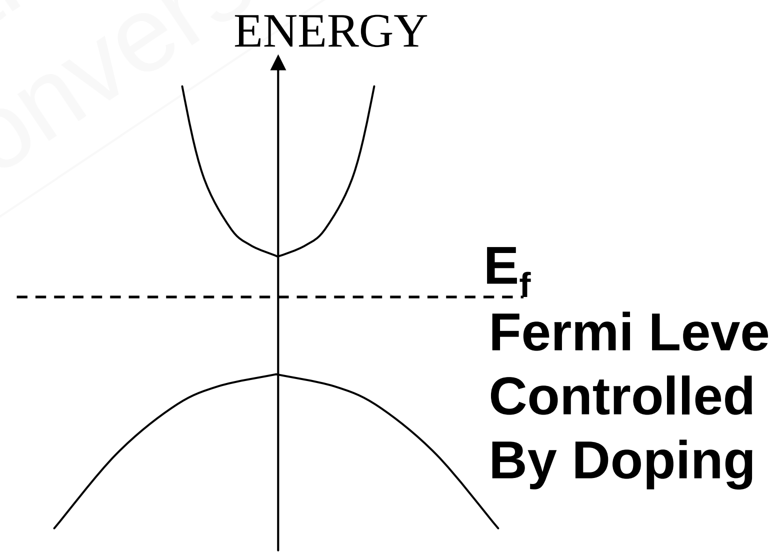
Semiconductor

$$S \propto \frac{1}{qT}\frac{\int \tau \mathbf{v}^2 D(E)(E-E_F)(-\partial f_{eq}/\partial E)dE}{\int \tau \mathbf{v}^2 D(E)(-\partial f_{eq}/\partial E)dE} \propto \langle E-E_f \rangle$$

Density of States

$$\sigma \propto \int \tau \mathbf{v}^2 \mathrm{D(E)}(-\partial f_{eq}/\partial \mathrm{E})\mathrm{dE}$$





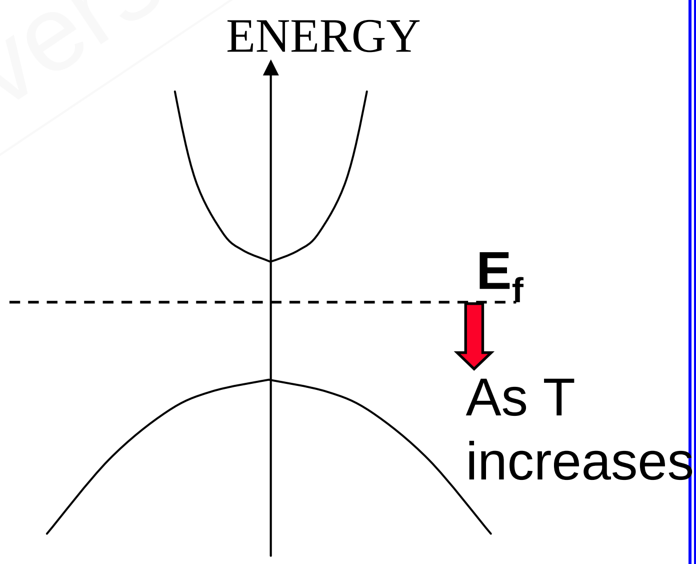
Boltmzann Statistics Results

$$\tau \propto (E - E_c)^{\gamma}$$

$$S = -\frac{\kappa_B}{e}\left[\frac{E_c - E_f}{\kappa_B T} + \left(\gamma + \frac{5}{2}\right)\right]$$

$$S = -\frac{\kappa_B}{e}\left[\ln\left(\frac{N_c}{n}\right) + \left(\gamma + \frac{5}{2}\right)\right]$$

$$N_c = 2\left(\frac{2\pi m^* \kappa_B T}{h^2}\right)^{3/2}$$



S increases with temperature!

Multiple Bands

$$S = \frac{S_a \sigma_a + S_b \sigma_b}{\sigma_a + \sigma_b}$$

$$k = k_L + k_a + k_b + (S_a - S_b)^2 T \frac{\sigma_a \sigma_b}{\sigma_a + \sigma_b}$$

Bipolar contribution

Property Examples

Images removed due to copyright restrictions.
Please see Fig. 2a,b in Poudel, Bed, et al. "High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys." *Science* 320 (May 2, 2008): 634-638.

$$\sigma = \frac{e^2}{3}\int \tau \mathbf{v}^2 \mathrm{D(E)}(-\partial f_{eq}/\partial \mathrm{E})\mathrm{dE}$$

$$\propto \left(\mathrm{k_B}T\right)^{\gamma+3/2} \exp\left(-\frac{E_c-\mu}{k_B T}\right)$$

For nondegenerate semiconductor only

- **Optimal thermoelectric materials are usually degenerate**
- **Multiband transport important at high temperatures, leading to decreasing Seebeck coefficient with increasing temperature**

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